FINAL THESIS

EXPERIMENTAL STUDY OF REACTIVITY AND MORPHOLOGICAL CHANGE OF FE-BASED CHEMICAL LOOPING PARTICLE IN CYCLIC REDUCTION-OXIDATION REACTIONS

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Abstract

Coal, an abundant and stable energy source, is playing an important role in current and future global energy supplies. Therefore, there is intensive research currently focusing on coal-conversion in a high-efficiency and environmentally-friendly way. The Chemical Looping Processes (CLPs) developed at The Ohio State University, can achieve H_2 and power generation from coal with 100% CO_2 capture. It uses Fe-based particles (Fe_2O_3) as oxygen carrier to capture and release oxygen in a cyclic manner, while coal-derived syngas ($CO + H_2$) can be converted into high-temperature heat for power generation with 100% CO_2 capture. It is widely believed that particle sintering is the main reason that cause of morphological deterioration and reactivity decay of pure Fe_2O_3 solids. Hence, most current efforts are put on anti-sintering and optimization of reaction condition. In this study, the exact solid deactivation mechanism was explored in order to achieve optimal particle development strategies. Reaction time, reaction temperature, and reduction-oxidation reaction cycle were the three factors studied to examine their individual effects on the resulting solid properties. The data showed that longer reaction time, lower reaction temperature, and multiple cyclic reactions would decrease a particle's surface area, pore volume, and corresponding reactivity. This structural change is a complex process which involves multiple factors in the cyclic reaction, such as the solid's inherent properties, solid-phase ionic transfer, and reaction condition. This study provides a better understanding of the deactivation mechanism of Fe-based chemical looping particles. It also has a pronounced influence and instructive significance to the future of particle development.

Keywords: Chemical Looping Processes (CLPs), CO_2 capture, Fe-based particles (Fe_2O_3), cyclic reactions, morphological deterioration, reactivity decay, reduction-oxidation reaction.

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Introduction

Energy is a significant issue all over the world. With the rapid development of technology and industry, the world is getting increasingly dependent on energy resources. Among all kinds of energy sources, crude oil and other fossil fuels are currently the dominant energy sources. However, considering the high crude oil price and unstable supplies, other fossil fuels should play a more important role in future's global energy supplies, such as coal, an abundant and stable energy source.[1] Therefore, there is now intensive research focusing on coal-conversion in a high-efficiency and environmentally friendly way.

The chemical looping processes (CLPs) developed at the Ohio State University (OSU) can achieve H_2 and power generation from coal with 100% CO_2 capture. One important type of chemical looping process is the Syngas Chemical Looping process (SCL). It uses Fe-based particles as oxygen carrier to capture and release oxygen in a cyclic manner, while coal-derived syngas ($CO + H_2$) can be converted into high-temperature heat for power generation with 100% CO_2 capture.[2, 3] The theory of Fe-based Chemical Looping Process is illustrated in figure 1 below.

Reduction: $Fe_2O_3 + C_xH_yO \rightarrow Fe + H_2O + CO_2$

Oxidation: $O_2 + Fe \rightarrow Fe_2O_3$

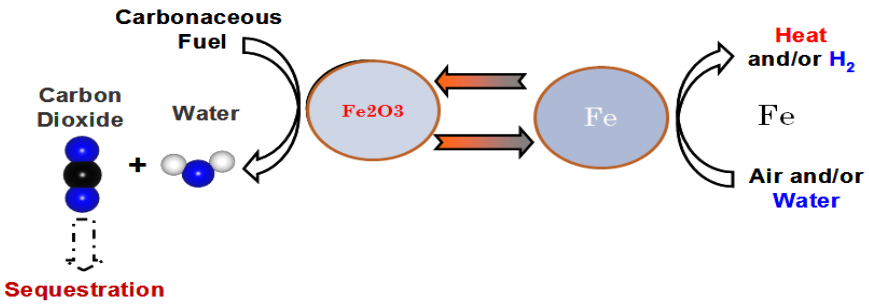

Figure 1 illustration of Fe-based Chemical Looping Process

In this process, Fe_2O_3 can be converted to Fe by the reduction reaction with carbonaceous fuel, while Fe can be oxidized back to Fe_2O_3 by reacting with O_2 (air). In the meantime, products of this reduction-oxidation reaction are pure carbon dioxide and water. After a separation with water, the pure carbon dioxide will undergo further sequestration to achieve 100% capture.

Background

During a chemical looping process, there is an important type of reaction called gas-solid reaction. It is a ubiquitous chemical process in our daily life, no matter in modern industries or natural environment. In a gas-solid reaction, the solid reactants can chemically absorb/release/exchange components from/to/with the gas reactants, respectively. One of the most important factors that characterize a gas-solid reaction is the solid surface structure that significantly affects the reaction rate and the resulting solid properties. A solid surface can be generally regarded as a combination of flat, convex, and concave structures. It is known that such surface structures vary in the course of reactions by the following three major mechanisms.

The first one is called mechanical interaction. In some reactions like hydration of CaO, the reaction-induced physical force would mechanically affect the surface structure, leading to surface cracking in most cases. The second mechanism is the molar volume change. If the molar volume of the solid product is larger than that of the solid reactant, the expansion of solid "molecules" narrows the inter-solid distance, thereby closing surface concave structures. If the solid product has a smaller molar volume than the solid reactant, the surface concave structure would be enlarged. Heat-induced sintering is the third mechanism. When the gas-solid reaction occurs at a high temperature, the sintering effect tends to smooth the solid surface by "transporting" solid species from surface convex structures to concave structures under the driving force of surface-energy gradient. These three major mechanisms dominate people's understandings of solid surface structure variation during gas-solid reactions in the past decades.

Based on the dominating solid-phase ionic transfer mechanism, a gas-capture reaction can be categorized into "inward diffusion mode," "outward diffusion mode," or "mixed diffusion

mode."[4,5] The ionic diffusion during the corresponding gas-release step is generally a reverse process of the capture-step in principle. In the "inward diffusion mode," the structural ions (*e.g.* Ca^{2+} in $CaO/CaCO_3$) which define the solid structure, do not change by the inward and outward diffusion of the non-structural ions (*e.g.* CO_3^{2-} in $CaO/CaCO_3$).[7] While in both "outward diffusion mode" and "mixed diffusion mode," the structural ions (*e.g.* iron cation in Fe/FeO_x) diffuse though the solid surface.[3]

The inert marker experiment is a simple and useful method to determine dominating ionic diffusion mode in solid gas reactions. This method uses a piece of inert material (*e.g.* Pt) as a marker on the surface of solid reactant. The inert material does not dissolve into either gas or solid phase. Therefore it can mark the initial gas-solid interface throughout the entire reaction process. The principle of the inert marker experiment is illustrated in the figure 2.

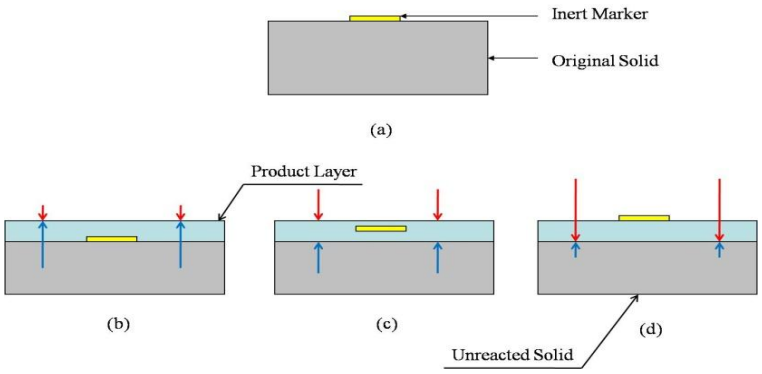

Figure 2 Principle of inert marker experiment to determine the dominating ionic

After conducting three different gas-solid reactions, sample (b) proves an outward diffusion mode of reaction, while sample (c) is a mix diffusion mode and sample (d) has an inward diffusion mode.

However, a large number of gas-solid reactions undergo outward diffusion of solid species such as oxidation of pure iron. If a gas-solid reaction involves outward ionic diffusion of

solid species, the solid surface tends to be smoothed by this reaction-induced diffusion process. Specifically, the surface concave structure is buried and the height of surface convex decreases. This phenomenon should occur and only occur in the gas-solid reactions involving outward ionic diffusion of solid species. [6]

To better understand the following experiment, a typical pure iron oxidation process at the dense grain level is shown in figure 3. It can be seen that iron diffuses from the pure iron phase through the initial gas-solid interface onto the gas-solid interface to react with oxygen gas. As a result, the iron oxides layer grows outward at the gas-solid interface. Because of the outward diffusion of iron, the lattice vacancies would form in the iron phase, which then agglomerate into a porous-iron structure. As the reaction proceeds, the interface of porous iron and dense iron migrates inward into the solid interior.

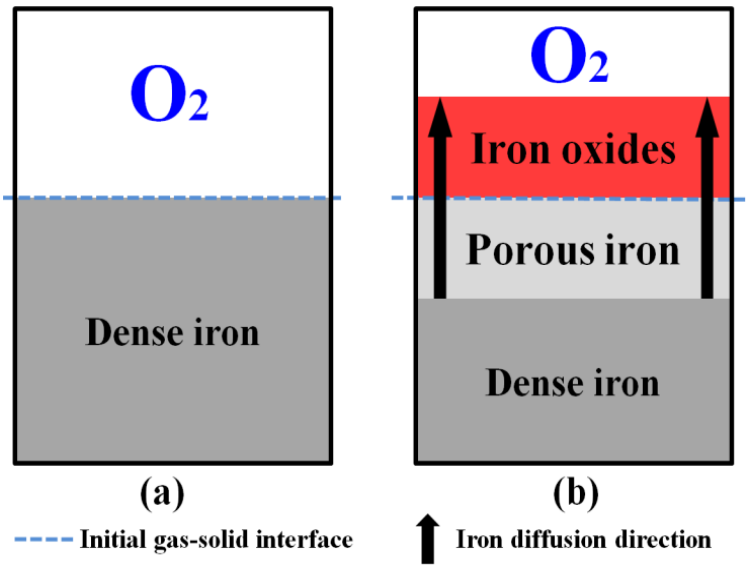

Figure 3 Solid-layer distribution and solid-phase ionic diffusion in pure iron oxidation.

(a) before oxidation; (b) after partial oxidation

Experimental Design

It was widely reported that the morphological property and reactivity of pure Fe_2O_3/Fe solids deteriorate steadily, reason of which is mostly attributed to the particle sintering at high temperatures. Sintering tends to transform smaller particles into larger ones and fill up the pore structure. Therefore, much previous work put efforts forward the enhancement of initial solid morphological properties, anti-sintering, and optimization of reaction condition.[2, 8] These efforts are only effective in a very limited number of reduction-oxidation (redox) cycles. However, as the number of reaction cycles increases, the reactivity and morphological properties deteriorate eventually. Therefore, it is necessary to understand the exact solid deactivation mechanism for the best particle development strategies.

This research project aims at studying other unknown factors that may change the reactivity and morphological properties of Fe-based chemical looping particles in addition to the widely known sintering mechanism. Therefore, 1) reaction time, 2) reaction temperature and 3) reduction-oxidation reaction cycle are going to be independently examined with respect to their effects on the resulting solid properties. By studying possible effects that have on reactivity and morphological properties change of Fe based particles, we can have a better understanding of the deactivation mechanism of Fe-based chemical looping particles. It also has a pronounced influence and instructive significance to the future particle development.

A Perkin-Elmer (Pyris 1) thermogravimetric analyzer (TGA) apparatus was used to prepare and test the Fe/ Fe_2O_3 solids. 40 mg Fe_2O_3 powder was used in each test as a starting sample. The total air flow rate for oxidation reaction was 200 ml min^{-1}, which consists of about 21% O_2 and 79% N_2. The gas stream for reduction reaction consists of 30 ml min^{-1} H_2 and 150

ml min^{-1} N_2. The reaction condition for sample preparation steps (α and β sections in Figure 1) is illustrated in Table 1. The resulting reactivities of Fe solid reactants after the preparation steps at 800 ^oC or 900 ^oC are tested at 900 ^oC in an air stream. The sample weight is continuously recorded for further analysis.

In order to identify the independent roles of reaction temperature, reaction time, and reduction-oxidation cycle to the resulting reactivity and morphological changes of Fe solid in the cyclic Fe-O_2 reaction, five representative samples are prepared and tested by TGA. Detailed information of sample preparation procedure was listed in Table 1. All the five samples are prepared and tested through the cyclic reaction process shown in Figure 4.

Table 1 Detailed information of the five representative samples in TGA test

Sample I.D.	**Initial Reduction (α)**	**Reduction-Oxidation (Redox) Cycles (β)**			
		1st Oxidation	**1st Reduction**	**2nd Oxidation**	**2nd Reduction**
Fresh Fe	Stops after reduction completes	N/A	N/A	N/A	N/A
Sintered Fe (Sintering + 0 Redox)	20min-260min	N/A	N/A	N/A	N/A
Sintering + 1 Redox	20min-30min	30min-70min	70min-260min	N/A	N/A
Sintering + 2 Redox	20min-30min	30min-45min	45min-70min	70min-120min	120min-260min
Sintered Fe_2O_3	N/A	N/A	230min-260min	N/A	N/A

The morphological properties of Fe samples are tested in a NOVA 4200e analyzer (Quantachrome Company). The Brunauer Emmett Teller (BET) surface area, pore volume, and pore size distribution were measured at -196 ^{o}C using liquid N_2 as an adsorbent.

The Fe's gas capture capacity can represent its reactivity. It is calculated by the weight capture percentage after 5 minutes oxidation at 900 ^{o}C as shown below.

Weight Capture Percentage: $C_t = \frac{(W_t - W_o)}{W_0} \times 100$ (%);

Where W_o (mg) is the sample weight after complete reduction. W_t (mg) is the sample weight after 30 after 5 minutes' oxidation n (for Fe). Therefore, a larger weight capture percentage C_t refers to a higher gas capture reactivity of a solid reactant.

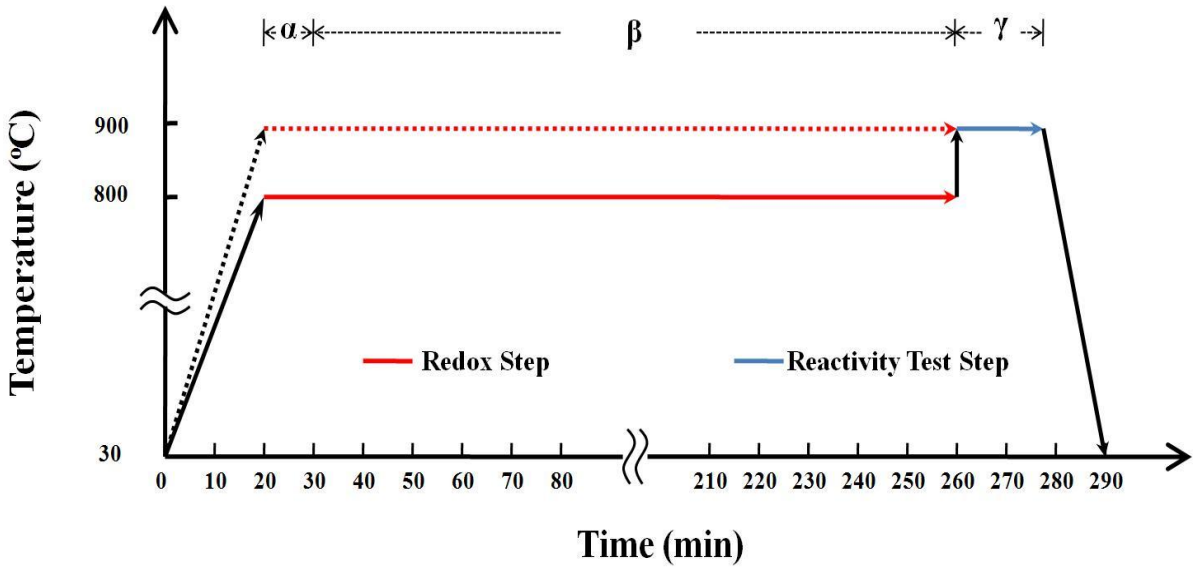

Figure 4 Schematic illustration of temperature sequence of Fe sample preparation and test.

(α: initial reduction; β: Redox cycles; γ: final test).

The effect of reaction time is studied by varying the reaction time length. The "Fresh Fe" sample is obtained immediately after the reduction reaction between Fe_2O_3 and H_2 at 900 ^oC completes. As a comparison, another sample, "Sintered Fe," will be obtained after going through an extended 900^oC temperature condition at H_2 without any further redox reactions. Both samples' weight capture percentages in 30 min are tested by TGA at the same condition (900 ^oC) to compare the reactivity changes. Also, the surface area and pore volume of these samples are tested by BET.

800 ^oC and 900 ^oC are compared to study the effect of reaction temperature on Fe. With other parameters fixed for a given solid, the difference in the resulting solid reactivity is caused by the temperature difference during the previous reaction step. All five samples are prepared and tested under 800 ^oC and 900 ^oC. Their reactivities and morphological properties (surface area and pore volume) are compared between two different temperatures.

With the reaction temperature and reaction time being fixed, the temperature-induced sintering effect on Fe particles should be the same. Therefore, the effect of a redox reaction cycle can studied by comparing among "sintered Fe + 2 redox" sample which goes through 2 redox reaction cycles, "sintered Fe+1 redox" sample which just goes through 1 redox reaction cycle, and "sintered Fe" which only goes through the same time and temperature condition without any reactive gas introduced. Still, the reactivity and morphological properties of these three samples are tested by TGA and BET.

Results and Discussion

Effect of Reaction Time

As shown in Figure 5, the "Sintered Fe" ("Sintering + 0 Redox") has lower reactivities than the "Fresh CaO" and "Fresh Fe". With a longer duration, sintering would have a greater deteriorating effect on a solid particle, which agglomerates smaller particles and fuses pores to a higher level. This greater sintering effect at a longer duration is reflected on the particles' lower surface areas and pore volumes. (see Table 2)

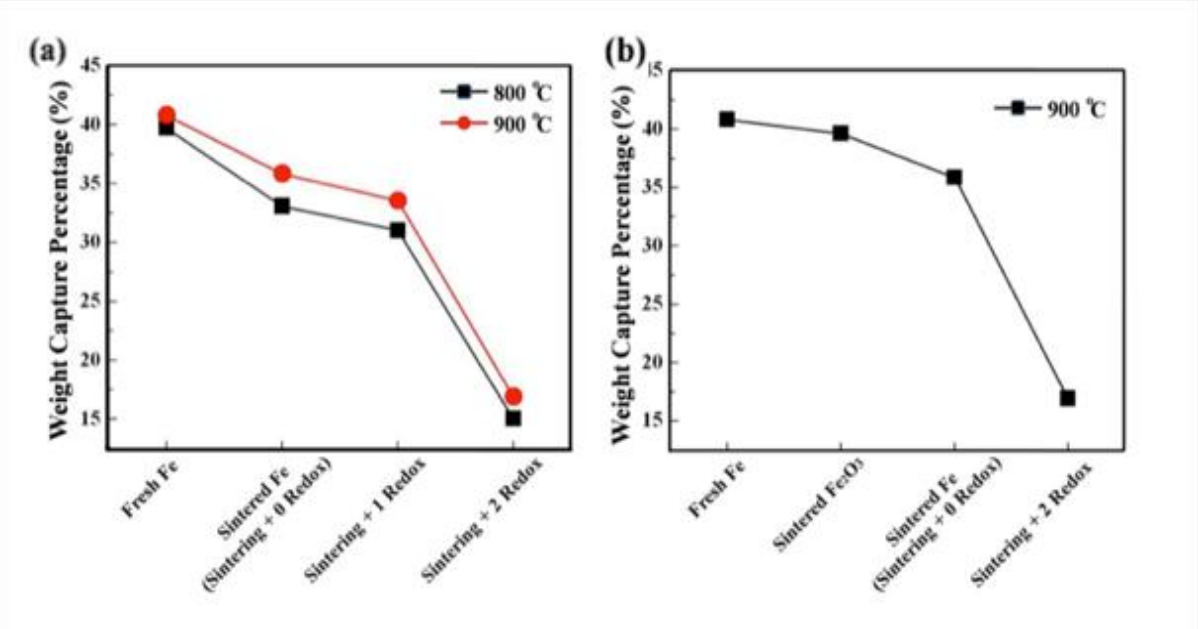

Figure 5 Effects of reaction time, reaction temperature, and cyclic reactions on the gas-capture capacities (reactivities) of Fe (a): 5 min O2 weight capture percentage of Fe; (b): control test of sintered Fe2O3

Effect of Reaction Temperature

As can be seen in Figure 5, the resulting Fe's reactivity after the 800 ^{o}C reaction is higher than that after 900 ^{o}C reaction. The corresponding morphological properties show the same trends. (Table 2) This temperature effect goes against the conventional belief that higher reaction temperature will lead to lower reactivity and worse morphological properties because of an increased sintering effect. [2, 6, 8] If the temperature is too high, the sintering effect can destroy the pore structure and ruin the solid reactivity. However, if the reaction temperature is not too high to play a dominant role on the deteriorating effect, other factors can determine the overall temperature effect on the solid properties in a cyclic gas-solid reaction.

It is known that the cyclic gas-solid reactions can be affected by 1) molar volume expansion-and-shrinking process and 2) diffusion of structural ions. In the gas-capture process, the molar volume of the solid product is higher than that of the solid reactant. The product layer swells and pores are "squeezed" off as the reaction proceeds." [3] When the gas component is released by the solid product, pores are regenerated. This molar volume expansion-and-shrinking process is mainly determined by the inherent properties of the solid product and the solid reactant, which are only slightly affected by temperature. In this study, the dominating solid-phase ionic transfer mechanism during the gas-capture step follows the "outward diffusion mode" or "mixed diffusion mode." [6] Iron cations diffuse outward through the gas-solid interface during the capture-step which adds extra volume expansion, and diffuses inward during the gas-release process which adds extra pore generation. Since a higher temperature would increase ionic diffusivity, it would generate better morphological properties through enhanced volume expansion and shrinking processes especially in the Fe's O_2 capture capacity, as shown in table 2.

Table 2 Morphological information of Fe solid rectants

Sample I.D.	Surface Area (m^2/g)	Pore Volume (cc/g)
Fresh Fe @ 900 ^oC	2.605	2.782×10^{-3}
Sintered Fe (Sintering + 0 Redox) @ 800 ^oC	0.793	1.302×10^{-3}
Sintered Fe (Sintering + 0 Redox) @ 900 ^oC	1.111	1.246×10^{-3}
Sintering + 1 Redox @ 900 ^oC	0.754	1.444×10^{-3}
Sintered Fe_2O_3 @ 900 ^oC	1.796	1.837×10^{-3}

Effect of Cyclic Redox Reactions

By comparing Fe that goes through a cyclic redox reaction with Fe that only goes through the same temperature condition without any reactive gas introduced, it can be seen that cyclic redox reaction itself shows an obvious deteriorating effect on the resulting solid reactivity. And this deteriorating effect increases as the number of cyclic reaction increases. (Figure 2) To exclude the possibility that this effect is due to sintering on Fe_2O_3, Fe_2O_3 goes through the same temperature condition before being converted to Fe. As shown in Figure 5, the reactivities of "Sintered Fe_2O_3" and "Sintered Fe" are both higher than that of "Sintering+2 Redox". This shows that the cyclic redox reaction is an independent deactivating effect in the overall solid deterioration.

In the gas-solid reaction between Fe and O_2, the structural ions would diffuse outward through the gas-solid interface. This outward diffusion rate is almost equal everywhere on the flat surface and its direction is perpendicular to the gas-solid interface. While on the surface with curvature, like the "valley" area, the outward diffusion is greatly facilitated since the curvature

gives a larger diffusing surface pointing to the pore valley.[8] Because of this mechanism, the structural ions would diffuse more into the "valley" of pores than that to the "top" of pores, which leads to the pore burial. A reverse process occurs, when the gas component is released from the solid product and the structural ions diffuse backward. The effect of structural ion diffusion to pore structure was simulated by a 2-D continuum diffusion model, using a reduction and oxidation cycle of metal (usually the outward diffusion mode) as an example. It can be seen from Figure 6, that as the structural ions diffuse outward during the gas-capture, the pore depth decreases and the solid boundary expands. And as the structural ions diffuse inward during the gas-release, the pore depth increases and the solid boundary draws back.

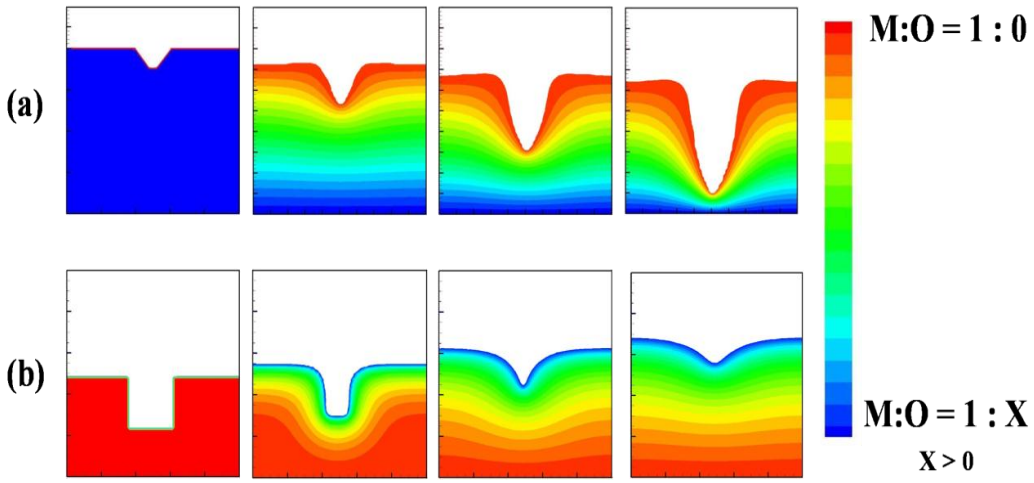

Figure 6 Illustration of the simulated pore structure change by diffusion of structural ions (e.g. iron cation in this study) in (a): gas-release (reduction) and (b): gas-capture (oxidation) cycles of metal "M"(Fe) using a 2-D continuum diffusion equation. [4]

This mechanism can also be shown from data in Figure 7. As Figure 7 shown, there is a general trend of pore volume changing from larger ranges to smaller ranges. Since smaller pores are generally more difficult to insert during the redox reaction, a cyclic redox reaction can generally deteriorate the morphological properties and reactivity of a solid reactant such as Fe.

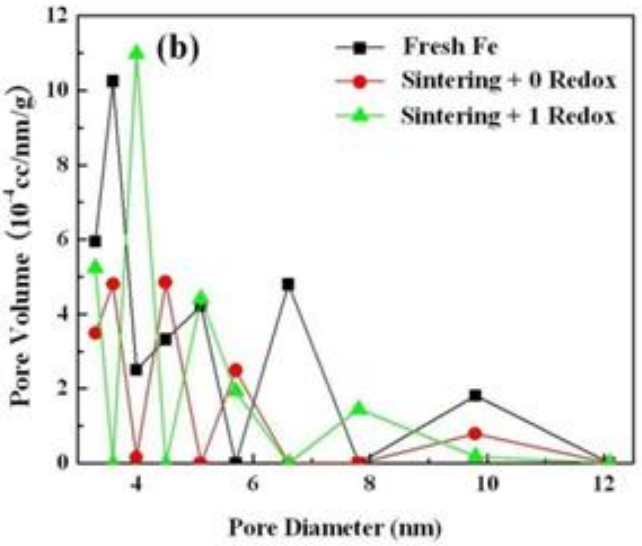

Figure 7 Pore size distributions of the tested Fe solids

Conclusion

In this study, the reactivity and morphological change of Fe-based chemical looping particle is explored. Fe reactivity is studied through its gas-capture capacity by Thermal Gravimetric Analysis (TGA). The morphological properties are characterized by the surface area and pore structure from BET tests. Cyclic reduction-oxidation reactions of Fe are used as a case in this study. Effects of reaction temperature, reaction time, and cyclic redox reaction on the solid reactivity and morphological properties are examined independently. It is found that longer exposure to reaction temperature would decrease the surface areas, pore volumes, and corresponding reactivities of Fe solids. The effect of reaction temperature on the reactivity of Fe solid is composite with previous perspective. Due to the dominating diffusing ions in the cyclic reaction, a higher reaction temperature induces greater sintering, which leads to a greater solid reactivity deterioration. With the effects of reaction temperature and reaction time excluded, the effect of a cyclic redox reaction is independently examined, which shows obvious deterioration to the Fe solids. It is found that diffusion of iron cations would bury the surface pore during the gas capture process. Elucidation of the mechanism of reactivity and morphological change of solid reactants would help re-evaluate the previous research efforts and re-build fundamental understandings of the cyclic gas-solid reactions.

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